

## METHOD FOR CLEANING OBJECTS

**[0001]** This invention relates to a method for cleaning objects and materials made from metal, glass, ceramics, plastic(s), or composites thereof or of textiles.

- 5 **[0002]** Cleaning methods, in which a vapor produced by heating an active cleaning liquid is brought into contact with the to-be-cleaned objects, are employed in the cleaning of a very wide variety of articles, such as metal objects, industrially-manufactured objects, such as printed circuit boards, articles of clothing, etc., of undesired contaminants, such as greases, lapping and polishing pastes, soldering pastes, adhesives, mixtures of inorganic (e.g., salty) fouling  
10 substances and organic fouling substances (e.g., consisting of greasy residues), etc. Until recently, chlorinated hydrocarbons were typically used for such cleaning tasks. But now, due to their lack of environmental compatibility, especially due to their ozone destruction potential, their carcinogenicity and their toxic effect, chlorinated hydrocarbons have been banned or are usable only under very strictly defined conditions. One advantage of using chlorinated  
15 hydrocarbons was that such substances do not have a flash point at commonly-occurring temperatures. Due to the above-noted disadvantages, chlorinated hydrocarbons have been replaced by other hydrocarbons or solvents, such as polypropyleneglycol ethers, alcohols, acetone, etc. The latter have a flash point in the range of normally-occurring temperatures and are thus ignition hazards. They also present another disadvantage in that they hardly remove  
20 pigment fouling or fouling having ionic salts, since these solvents only poorly dissolve pigments and/or salts due to their ionic character.

**[0003]** The object underlying the invention is to further develop a conventional cleaning method so that it is performable in an environmentally compatible manner while achieving a good cleaning effect.

- 25 **[0004]** Another object of the invention is to provide a new cleaning method, by which mixtures of inorganic and organic fouling can be simultaneously removed in an efficient manner. Another object of the invention is to provide a method for cleaning objects and materials made of metal that acts more gently than previously-known methods.

[0005] The previously-identified objects are attained by a method having the features of patent claim 1. Advantageous embodiments of the inventive method are found in patent claims 2 to 19.

[0006] According to the invention, azeotropic preparations, which are usable as active cleaning liquids, first have the advantage that their liquid phase effectively dissolves pigment fouling and fouling having ionic components, e.g., salts, due to the water proportion when the azeotropic preparation used as the active cleaning liquid comes into contact with the to-be-cleaned objects in the state of being a liquid. The molecules of the at least one additional component containing lipophilic groups, which additional component is preferably also a liquid under ambient conditions or at low treatment temperatures, ensure a good fat-dissolving capacity of the azeotropic preparation.

[0007] If the azeotropic preparation used as the active cleaning liquid is heated, both water and the other component(s) pass(es) into the vapor phase in a composition corresponding to the specific azeotrope due to its azeotropic character (for the definition of "azeotrope" see Römpps Chemie Lexikon [Römp's Chemical Dictionary], 9th Edition (1989), page 323). Upon contacting the vapor of the azeotropic preparation with the to-be-cleaned object, a reliable cleaning and "rinsing" of all fouling substances of the to-be-cleaned object removed by the cleaning process takes place.

[0008] It is particularly advantageous that the vapor is not combustible due its high water content. Precautionary measures in this connection are unnecessary in a device used for carrying out the inventive method. The flash point of the vapor, to the extent that such a flash point exists at all, is above the temperatures normally occurring in such a cleaning method, but is at least above the boiling point of the liquid and is advantageously above about 200 °C. A flash point above 200 °C is therefore of special advantage, because the precautionary measures to be taken when carrying out the cleaning method are less extensive than when using active cleaning liquids having lower flash points. The azeotropic preparation, which is present in the form of a vapor at least in a part of the inventive method, can be condensed into the liquid phase either on the to-be-cleaned object or by lowering the temperature, so that costly measures for protecting the atmosphere surrounding the device for carrying out the method, such as are required for conventional methods, can be eliminated to the greatest possible extent.

[0009] Hence, an additional advantage of the inventive method is the fact that the azeotropic preparation employed as the active cleaning liquid is scarcely consumed due to its recondensation to the greatest extent possible. A closed loop can thus be created in which the azeotropic preparation used as the active cleaning fluid need not be replenished at all or only in negligibly small amounts. This is additionally aided by making the inventive azeotropic preparation employed as the active cleaning liquid free of surfactants that precipitate on the filter surface during filtration of the active cleaning liquid for removing the fouling substances in conventional methods and require a replenishment in conventionally-used solutions.

[0010] Surprisingly, with the inventive method, complex types of fouling substances, such as dried body fluids or other fouling substances, which occur in everyday life as a result of deposition of fouling substances resulting from rain or snow, etc., are also removed from the to-be-cleaned objects.

[0011] The inventive method is not limited to closed systems. It can, for example, also be carried out in the form of open vapor stream cleaning.

[0012] When selecting the inventive azeotropic preparations employed as the active cleaning liquid and/or the other component(s) contained therein, which have molecules with hydrophilic groups (e.g., -OH, -NH<sub>2</sub>, -C-O-C-, -C(=O)-C-, -C(=O)-O, etc.) and lipophilic groups (e.g., CH<sub>2</sub>-chains or C<sub>1</sub>- to C<sub>12</sub>-alkyl-, etc.), in addition to good cleaning power, the following criteria stand in the foreground: The water content of the azeotrope of water and (a) further component(s) must be so high that there is no flash point and/or that the vapor is not combustible. The liquid and the vapor formed by heating the liquid may not be toxic or have an ozone destruction potential, nor may they cause a water hazard if the preparation is inadvertently released into the environment. Water-soluble components forming homogeneous azeotropes or also water-insoluble components forming heterogeneous azeotropes are suitable.

[0013] In a preferred embodiment, the inventive method for cleaning objects comprises the steps of:

-forming an azeotropic preparation from water and at least one component having molecules with hydrophilic and lipophilic groups in a weight ratio (component(s) with hydrophilic and lipophilic groups) : water of 0.05 to 99.5 : 99.95 to 0.05;

-bringing the to-be-cleaned objects first into contact with the azeotropic preparation and allowing the liquid azeotropic preparation to drain off, inclusive of the contaminants from the to-be-cleaned objects removed thereby;

-removing residues of the azeotropic preparation on and/or in the to-be-cleaned objects  
5 by evaporation; and

-condensing the vapor of the azeotropic preparation and using the azeotropic preparation recovered by condensation for a cleaning step once again.

[0014] Thus, it is accordance with a particularly preferred embodiment of the inventive method to bring the to-be-cleaned objects into contact at least once with the vapor of the  
10 azeotropic preparation and, during the duration of the contact, to allow the vapor of the azeotropic preparation to condense on the to-be-cleaned objects. For example, the to-be-cleaned objects can be first brought into contact with the liquid azeotropic preparation once or several times, for example by immersion, spraying, irrigation or by comparable methods known in the prior art of forcefully contacting with a liquid. The to-be-cleaned objects can subsequently be  
15 brought into contact one or more times with the azeotropic preparation in the form of the vapor thereof. The vapor of the azeotropic preparation thereby continuously condenses on the to-be-cleaned objects and carries away residues of contaminants removed from the to-be-cleaned objects as it drains off. As an alternative, however, the inventive method can be performed by bringing the to-be-cleaned objects into contact with a vapor of the azeotropic preparation at least  
20 once, preferably however several times. In this case as well, the vapor condenses during the duration of the contact on the to-be-cleaned objects and thereby removes the contaminants.

[0015] In an especially preferred embodiment of the method, an azeotropic preparation made from water and at least one component having molecules with hydrophilic and lipophilic groups is used, in which the weight ratio (component(s) with hydrophilic and lipophilic groups) :  
25 water is in the range of 1.0 to 35.0 : 99.0 to 65.0, and even more preferably is in the range of 4.0 to 15.0 : 96.0 to 85.0.

[0016] It is in accordance with another preferred embodiment of the inventive method to use an azeotropic preparation in the form of a mixture made from water and at least one additional component having molecules with hydrophilic and lipophilic groups as the active

cleaning liquid, wherein the additional component(s) and the water form an azeotrope at the phase transition liquid phase/vapor phase and the azeotrope is an azeotrope having an immiscibility gap at a temperature between 0 °C and the temperature of the phase transition liquid phase/vapor phase at standard pressure. Surprisingly, it has been found, in particular, that the azeotropes having immiscibility gaps have particularly advantageous cleaning properties. An azeotrope having an immiscibility gap at a temperature ranging from 20 °C to 110 °C at standard pressure is particularly preferably used.

[0017] By the term "at standard pressure", atmospheric pressure (approximately 1 atm; about  $10^5$  Pa) is understood in the description and in the patent claims.

[0018] Without being committed to a theoretical explanation of the invention at this time, it has been found that azeotropic preparations, which can be used as an active cleaning liquid in the inventive method, are clear at low temperatures of, for example, 20 to 25 °C. In other words, the components are fully dissolved in each other. Defined ratios of the composition of the components in the mixed phase arise for each temperature. The phases, which are separated at an elevated temperature, can be converted into an emulsion, which appears milky, through appropriate method steps, such as preferably through exposure to ultrasound, through intensive movement by pump-transferring or agitation, etc. This emulsion has discontinuous droplets of the organic component(s) in a continuous aqueous phase. The emulsion has an excellent fat-dissolving capacity due to its content of organic components (having molecules with lipophilic groups); however, due to the continuous aqueous phase, it also dissolves water-soluble, e.g. ionic, contaminants, such as salts. With further increases of the temperature of the azeotropic preparation, it passes into the vapor phase, in which vapor phase the components are present in the special composition typical for the respective azeotrope. During condensation, the azeotropic preparation again migrates through the immiscibility gap; consequently, condensed vapor of the azeotropic preparation is present again in the form of the emulsion on the to-be-cleaned objects, which emulsion has excellent dissolving properties for oily contaminants as well as ionic contaminants.

[0019] In the light of the criteria indicated above, some organic components, which form homogenous azeotropes with water, are preferred for use as organic components in azeotropic preparations that are employed for carrying out the method according to the present invention.

As is readily ascertainable for experts in this technical field, the invention is nevertheless not limited to the preferred, azeotrope-forming compounds.

**[0020]** The preferred compounds can best be described by the following general formula:



wherein:

-  $R^1$  and  $R^3$  each represent: H independently of each other; straight-chain or branched saturated or unsaturated  $C_1$ - to  $C_{18}$ -alkyl groups, in which one or more nonadjacent  $-CH_2-$  groups can be replaced by  $-O-$ ; saturated or unsaturated cyclic  $C_1$ - to  $C_8$ -alkyl groups, in which one or more nonadjacent  $-CH_2-$  groups can be replaced by  $-O-$ ; hydroxy;  $C_1$ - to  $C_8$ -alkoxy; amino, wherein one or both hydrogen group(s) can be replaced by  $C_1$ - to  $C_8$ -alkyl groups; and

-  $X$  represents:  $-O-$ ;  $-C(=O)-$ ;  $-C(=O)-O-$ ;  $-NH-$ ;  $-NR^1-$ ;  $-N(-OH)-$ ; straight-chain or branched  $(C_1$ - to  $C_8)$ -alkylene groups, in which one or more nonadjacent  $-CH_2-$  groups can be replaced by  $-O-$ ; and  $n$  represents integers 1, 2, 3, etc.

**[0021]** In other words, the organic components of the azeotropic preparations, which are used in the method according to the present invention, can be selected from organic compounds that belong to the groups of alcohols, glycols, amines, ethers, glycol ethers, esters, ketones, and amino alcohols as well as N-heterocyclics or organic acids.

**[0022]** In a particularly preferred method, compounds of the general formula indicated above are used as (an) organic component(s) of the azeotropic preparation or as (an) additional organic component(s), in which  $R^1$  and  $R^3$  each independently represents saturated or unsaturated  $C_1$ - to  $C_{12}$ -alkyl groups, more preferably saturated or unsaturated  $C_1$ - to  $C_8$ -alkyl groups, in which one or more nonadjacent  $CH_2$  group(s) can be replaced by  $-O-$ , hydroxy,  $C_1$ - to  $C_8$ -alkoxy and unsubstituted amino groups or amino groups substituted with alkyl groups; and/or  $X$  represents  $-O-$ ;  $-C(=O)-$ ;  $-C(=O)-O-$ ;  $-NH-$ ;  $-NR^1-$ ;  $-N(-OH)-$ ;  $-OCH(R^2)-CH_2-$  (wherein  $R_2$  represents H or methyl); and  $n$  represents 1 or 2.

**[0023]** Specific examples of the groups represented by  $R^1$  and  $R^3$  are hydrogen, methyl, ethyl, n-propyl, i-propyl, n-butyl, sec-butyl, i-butyl, tert-butyl, n-pentyl, n-hexyl, n-octyl, furfuryl-2, tetrahydrofurfuryl-2, hydroxy, methoxy, ethoxy and propoxy. Specific examples of the groups represented by X are -O-; -C(=O)-; -C(=O)-O-; -NH-; -NR<sup>1</sup>-; -N(-OH)-; ethyleneoxy and propyleneoxy.

**[0024]** Even more preferred methods according to the present invention employ compounds of the general formula indicated above as (an) organic compound(s) of the azeotropic preparations or as (an) additional organic component(s), which component(s) are selected from the group:

- 10 - (C<sub>1</sub>- to C<sub>12</sub>-alkyl) - C(=O)-O - (C<sub>1</sub>- to C<sub>12</sub>-alkyl);
- (C<sub>1</sub>- to C<sub>12</sub>-alkyl) - O - (C<sub>1</sub>- to C<sub>12</sub>-alkyl);
- (C<sub>1</sub>- to C<sub>12</sub>-alkyl) - C(=O) - (C<sub>1</sub>- to C<sub>12</sub>-alkyl);
- (C<sub>1</sub>- to C<sub>12</sub>-alkyl) - [N - (H or C<sub>1</sub>- to C<sub>12</sub>-alkyl) (H or C<sub>1</sub>- to C<sub>12</sub>-alkyl)];
- HO-(CH<sub>2</sub>)<sub>1, 2 ... etc.</sub> - [NH<sub>2</sub> or NH(C<sub>1</sub>- to C<sub>12</sub>-alkyl) or N(C<sub>1</sub>- to C<sub>12</sub>-alkyl)<sub>2</sub>];
- 15 - H - [O - CH(H or CH<sub>3</sub>) - CH<sub>2</sub>]<sub>1, 2 ... etc.</sub> - OH; and
- (H or C<sub>1</sub>- to C<sub>12</sub>-alkyl) - [O - CH(H or CH<sub>3</sub>) - CH<sub>2</sub>]<sub>1, 2 ... etc.</sub> - [OH or O(C<sub>1</sub>- to C<sub>12</sub>-alkyl)].

- [0025]** Special examples of organic compounds, which can be used, either alone or collectively in groups of a plurality of the mentioned compounds, in azeotropic preparations of
- 20 the active cleaning liquid, are selected from propyleneglycol ether; dipropyleneglycolmonomethylether; dipropyleneglycolmono-n-propylether; tripropyleneglycolmonomethylether; 3-methoxy-3-methylbutanol; furfuryl alcohol; tetrahydrofurfuryl alcohol; 1-aminobutanol-2; monoisopropanolamine; 2-amino-2-methylpropanol-1; 2-amino-2-methylpropanediol-1,3; 3-(aminomethyl-)pyridine; ethanolamine;
  - 25 furfurylamine; methyl lactate; isopropyl lactate; aminoacetaldehydedimethylacetal; 4-aminomorpholine; 1-methylimidazole; 1,2-dimethylimidazole; 1-vinylimidazole; 1,4-

diazabicyclo[2.2.2]octane (DABCO); 1,5-diazabicyclo[4.3.0]non-5-ene; and 1,8-diazabicyclo[5.4.0]undec-7-ene.

5 [0026] It is in accordance with a further, also preferred, embodiment to add at least one cleaning booster, which does not independently vaporize, to the active cleaning liquid for the inventive method. It or they should preferably distill with the azeotropic preparation. Such cleaning boosters, which do not independently vaporize, are known to the skilled person from the prior art and therefore require no further enumeration at this time.

10 [0027] Likewise, it is preferable in accordance with the invention to add at least one corrosion prevention additive to the active cleaning liquid. It or they should preferably distill with the azeotropic preparation. Such corrosion prevention additives are particularly advantageous when objects made of nonferrous heavy metals or light metals should be cleaned. For example, aluminum articles can be cleaned with excellent results using an azeotropic preparation comprising 1-methylimidazole. It acts as an inhibitor. The cleaning of parts made of copper can also be carried out in an advantageous manner with azeotropic preparations  
15 comprising 1-methylimidazole. Brightening of the surface is achieved thereby. Instead of the above-mentioned compound, other corrosion prevention additives and corrosion prevention inhibitors can also be added, as are known to the skilled person from the prior art.

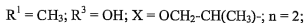
[0028] Especially preferred as yielding excellent cleaning results are methods for cleaning objects according to the invention, in which an azeotropic preparation made of water  
20 and an organic component is used as the active cleaning liquid. In this case, the organic component is preferably a compound that is selected from the group: dipropyleneglycolmonomethylether; dipropyleneglycolmono-n-propylether; tripropyleneglycol monomethylether; 3-methoxy-3-methylbutanol; furfuryl alcohol; tetrahydrofurfuryl alcohol; 1-aminobutanol-2; furfuryl amine; methyl lactate and isopropyl lactate.

25 [0029] The indicated compounds belong to the following groups of compounds having the general formula  $R^1-[X]_n-R^2$ :

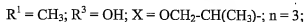
(A) Glycol ethers:

- organic component No. 1: dipropyleneglycolmonomethylether

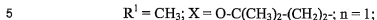




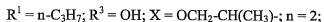
- organic component No. 2: tripropyleneglycolmonomethylether



- organic component No. 3: 3-methoxy-3-methylbutanol

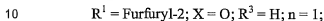


- organic component No. 4: dipropyleneglycol-n-propylether

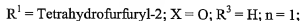


(B) Alcohols:

- organic component No. 5: furfuryl alcohol

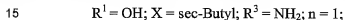


- organic component No. 5: tetrahydrofurfuryl alcohol

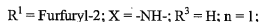


(C) Amines:

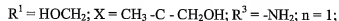
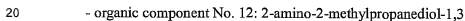
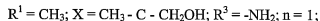
- organic component No. 7: 1-aminobutanol-2



- organic component No. 8: furfurylamine

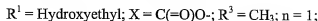


- organic component No. 11: 2-amino-2-methylpropanol-1



## (D) Esters:

- organic component No. 9: methyl lactate



- organic component No. 10: isopropyl lactate

5  $R^1 = \text{Hydroxyethyl}; X = C(=O)O-; R^3 = i\text{-}C_3H_7; n = 1;$

[0030] In such azeotropic preparations to be used as an active cleaning liquid in the inventive method, water and an organic component are present in relative amounts of (100 - x) wt% : x wt%. Herein, x is in the range of  $0 < x \leq 35$ , preferably in the range  $3 \leq x \leq 25$ , particularly preferably in the range  $4 \leq x \leq 15$ .

10 [0031] In another preferred method, the mixture ratio of water and the other component(s) in the azeotropic preparation is substantially set at the ratio, which is present in the vapor that results by heating the liquid azeotropic preparation.

[0032] In another, also preferred, embodiment, the inventive method for cleaning objects includes a step of using an azeotropic preparation made of water and two organic components as  
15 the active cleaning liquid. An azeotropic preparation made of water, dipropylene glycol mono-n-propylether and an additional organic component is particularly preferably used as the active cleaning liquid. In this embodiment, further components can also be contained in the azeotropic preparation employed as the active cleaning liquid, for example at least one cleaning booster, which does not independently vaporize and more preferably distills with the azeotropic  
20 preparation, as is known from the prior art and has already been mentioned above, and/or at least one corrosion prevention additive or corrosion prevention inhibitor (more preferably, one that distills with the azeotropic preparation), as is also known from the prior art and has already been mentioned above.

[0033] In accordance with this preferred embodiment, it is particularly preferred to use a  
25 compound from the following group as additional organic components: 1-aminobutanol-2; monoisopropanolamine; 2-amino-2-methylpropanol-1; 2-amino-2-methylpropanediol-1,3; 3-(aminomethyl)-pyridine; ethanolamine; aminoacetaldehydedimethylacetal; 4-aminomorpholine;

1-methylimidazole; 1,2-dimethylimidazole; 1-vinylimidazole; 1,4- diazabicyclo[2.2.2]octane (DABCO); 1,5-diazabicyclo[4.3.0]non-5-ene; and 1,8-diazabicyclo[5.4.0]undec-7-ene.

[0034] The mentioned organic compounds can be used alone or in combination with each other.

5 [0035] It is also particularly preferred to use an additional organic component from the group: acetic acid, hydroxyacetic acid, formic acid and butyric acid. The indicated acids can also be used alone or in combination with each other or with other substances, such as the organic components named above.

10 [0036] In accordance with the above-described preferred embodiment, an azeotropic preparation made of water, a glycol ether (preferably dipropylene glycol mono-n-propylether) and an additional organic component is used as the active cleaning liquid in relative amounts of 90 wt% : (10 - y) wt% : y wt%, wherein y is in the range of  $0 < y \leq 5$ , particularly preferably  $0 < y \leq 2$ .

[0037] A device, in which the inventive method can be carried out, is schematically illustrated in the appended Figure: A reservoir tank 2 having a precipitation chamber 4 and an overflow chamber 6 is connected via a feed pump 8 and a heating device 10 to a cleaning device 12. The interior of the cleaning device, whose structure is known in the prior art and which can include cleaning nozzles, a circulating basket, etc., is connected, in the example shown in the Figure, to a pressure compensation vessel 14, which is however not essential for operation.

20 [0038] A conduit leads from the bottom of the cleaning device 12 to a filter device 16. The filter device 16 is connected via a conduit with a feed pump 18 on the top side of the precipitation chamber 4. Another conduit leads from the filter device 16 back to the precipitation chamber 4 via a vacuum pump 20 through a condenser 22 and a cooler 24.

[0039] A conduit further leads from the overflow compartment 6 into a distillation device 30 via a feed pump 26 through a heat exchanger 28 and from there into the cleaning device 12 or back to the reservoir tank 2.

[0040] A feed line 32 leads into the reservoir tank 2 for filling the reservoir tank 2 with the active cleaning liquid. The reservoir tank 2 also contains a not-illustrated device for drawing off sludge that deposits in the precipitation chamber 4.

[0041] Ventilation piping 34 leads into the normally-sealed cleaning device 12.

5 [0042] The structure of the individual structural elements of the described cleaning device 12 and an electronic control (not shown) of the individual assemblies are known and are therefore not described in detail.

[0043] The function of the described device is as follows: After charging the cleaning device 12 with a to-be-cleaned item, a liquid cleaning takes place in an exemplary but not restrictive embodiment, in which the feed pump 8 is actuated and the active cleaning liquid, the temperature of which can be adjusted in the heating device 10 if necessary, is fed into the cleaning device 12. An immersion bath of the circulating cleaning item and/or a spraying of the cleaning item with liquid takes place in the cleaning device 12. The liquid is removed from the cleaning device 12 through the filter device 16 by the feed pump 18 and is fed into the precipitation chamber 4. Predominantly inorganic fouling substances precipitate in the filter device 16 and are drawn off. Predominantly fat-containing fouling substances precipitate in the precipitation chamber 4 and are also drawn off.

[0044] The exemplary-described liquid cleaning stage is followed by rinsing under the same conditions with active cleaning liquid from the tank 6.

20 [0045] Then, a vapor cleaning stage and/or a vapor rinsing stage takes place, in which the feed pump 26 is actuated so that the active cleaning liquid is heated in the distillation device 30 and is converted into vapor. As a consequence of the azeotropic character of the azeotropic preparation employed as the active cleaning liquid, this vapor has a predetermined content of water and the additional component(s). The liquid azeotropic preparation is preferably already  
25 composed from its components so that they also correspond to the content to the corresponding components in the vapor phase. In the cleaning device 12 the vapor comes into intensive contact with the to-be-cleaned item, wherein at least a part of the vapor condenses. The condensate is supplied by feed pump 18 to the precipitation chamber after flowing through the filter device 16.

[0046] When the vapor is fed back into the reservoir tank 6 from the distillation device 30 via the condenser 22 and the cooler 24, the liquid can be purified thereby.

[0047] The vapor cleaning or vapor rinsing is advantageously followed by recirculating drying or vacuum drying. The vapor present inside the cleaning device 12 is thereby suctioned off by the vacuum pump 20, wherein the condensate formed in the cleaning device 12 flows through the filter device 16. The vapor mixed with the condensate is again supplied to the reservoir tank 2 as a liquid after flowing through the condenser 22 and cooler 24.

[0048] After vacuum drying has been completed, the precipitation chamber 4 is ventilated via the ventilation line 34, and the cleaned item can be removed.

[0049] In an alternative embodiment, which also yields favorable results, to-be-treated objects are sprayed in the cleaning device 12 with the azeotropic preparation used as the active cleaning liquid. This happens in the way that the to-be-cleaned objects are saturated with the liquid. The subsequent method steps are essentially the same as were described above.

[0050] After the treatment, the to-be-treated objects are in a distinctly better condition than after treatment in a conventional method, i.e. by using customary solvents for the cleaning steps under identical conditions. In particular, it has been surprisingly determined that not only are all organic fouling substances, inclusive of lipophilic and/or oily or fatty substances, removed, but also all the inorganic fouling substances, in particular inorganic salts from perspiration, color pigments, etc. The treated objects have no unpleasant odor and exhibit an excellent appearance.

[0051] As was already explained above, azeotropic preparations having an immiscibility gap exhibit a surprisingly good cleaning behavior distinctly superior to that of conventional preparations.

[0052] In the case of using azeotropic preparations having an immiscibility gap, the to-be-cleaned objects are brought into contact with an azeotropic preparation when treating in the liquid phase, which azeotropic preparation is in a state, in which the components of the azeotropic preparation are present in separate, or at least partly separate, phases. For example, the liquid azeotropic preparations present in the state of phase separation are treated with

ultrasound or are intensively pump-transferred or agitated, so that a milky emulsion of the azeotropic preparation forms. This emulsion effectively dissolves not only fatty or oily components, but also ionic and/or salty contaminants.

5       **[0053]**        In the case of treating to-be-cleaned objects with the azeotropic preparation in the vapor phase, the azeotropic preparation is heated as previously described and a vapor is produced, in which the components are present in the quantitative proportions that are determined by the characteristic azeotropic properties. The vapor condenses at least partially on the to-be-cleaned objects, and the same milky emulsion arises as in the liquid phase. An excellent oil- and salt-dissolving capacity is also observed in this case.

10       **[0054]**        By increasing the temperature of the azeotropic preparation to the phase transition liquid phase/vapor phase, the components pass into the vapor phase in the quantitative proportion corresponding to the azeotrope, and the azeotropic preparation can be purified by distillation without problem.

15       **[0055]**        The last-mentioned embodiment of the inventive method is particularly advantageous for cleaning metal parts. Thus, for example, lapping and polishing pastes can be highly effectively removed from metal parts by using azeotropes having an immiscibility gap. For instance, an azeotropic preparation mixed with acidic additives is used as the active cleaning liquid for this purpose. The cleaning takes place in the above-described one chamber system and can take place continuously or in a batch process.

20       **[0056]**        Likewise, SMD adhesives (SMD = surface mounted devices), such as are employed in the manufacture of SMD components for double-sided mounting, can also be removed surprisingly well from electronic components, whereby the components do not detach during the soldering process. The adhesive is usually applied via dispenser systems or templates before the printed circuit boards are attached. Defectively-printed/dispensed circuit boards  
25 and/or templates can be cleaned. Surprisingly, cleaning results can be achieved with the azeotropic preparations employed according to the invention that distinctly surpass those achieved with conventional solvents such as butyl acetate or isopropanol. In addition, precautionary measures (such as those taken to prevent explosions when correspondingly hazardous solvents are used) are unnecessary.

[0057] In the same way, surplus soldering paste applied during soldering can be removed from defectively-printed boards and templates in a simple and environmentally-friendly manner. The removal of fluxing agent residues after soldering is likewise possible. The cleaning takes place by spraying, spray rinsing, and drying of the to-be-cleaned objects, preferably in the immersion process with ultrasound (cleaning stage), rinsing with or without ultrasound (rinsing stage) and drying. The cleaning is carried out preferably at a temperature in the range of 40-60 °C, but it is not restricted to this temperature range. The temperature may be significantly higher, for example, it may even exceed 100 °C, in particular when treating the to-be-cleaned objects during the cleaning stage with the vapor of the azeotropic preparation.

[0058] Particularly preferably, the azeotropic preparations according to the following Table I are used for cleaning methods according to the invention. The preferred proportions of organic components (O.C.) : water, the boiling points of the respective azeotropic preparations, as well as the temperatures, at which to-be-cleaned objects can be treated in an exemplary manner, are provided in this Table. The invention is not, of course, restricted to the proportions of the indicated components and treatment temperatures.

[0059] In the case of using azeotropes having an immiscibility gap, three-component-mixtures made of water, dipropylene glycol mono-n-propylether, and amine compounds and/or N-heterocyclic compounds or organic acids according to the following Table II are particularly preferably used. An exemplary, but not limiting, composition of the azeotropes is as follows: water (90 wt%), dipropylene glycol mono-n-propylether (10 - y wt%), y wt% of the compounds indicated in Table II.

[0060]

Table I

Azeotropic Preparation		Boiling Point (°C)	Treatment Temperature (°C)
Organic Components (O.C.)	Ratio O.C. : Water		
No. 1	8.9 : 91.1	99.2	60
No. 2	7.9 : 92.1	99.1	60
No. 3	11 : 89	99 – 101	65
No. 4	10 : 90	100	65
No. 5	20 : 80	98.5	65
No. 6	10.5 : 89.5	102	65
No. 7	4.7 : 95.3	102	65
No. 8	30.9 : 69.1	100	60
No. 9	20 : 80	99.5	60
No. 10	34 : 76	98	60
No. 11	5 : 95	98	65
No. 12	6.5 : 93.5	101	60



[0061]

Table II

Organic Components	y (wt%)	Boiling Point (°C)
1-Aminobutanol-2	0.3	101
Monoisopropanolamine	0.8	100
2-Amino-2-methylpropanol-1	1.3	102
2-Amino-2-methylpropanediol-1,3	1.5	101
3-(Aminomethyl)pyridine	0.16	101
Ethanolamine	0.3	104
Aminoacetaldehyde-dimethylacetal	2.4 3.4 4.2	101
4-Aminomorpholine	0.4	101
1-Methylimidazole	0.1	101
1,2-Dimethylimidazole	0.1	100 – 102
1-Vinylimidazole	0.3	101
DABCO	0.03 0.08 0.1	101 – 103
1,5-Diazabicyclo[4.3.0]non-5-ene	0.02	101 – 103
1,8-Diazabicyclo[5.4.0]undec-7-ene	0.02	101 – 103
Acetic Acid (80%)	1.5	100 – 101
Hydroxyacetic acid	0.5	100 – 101
Formic Acid	1.5	100 – 101
Butyric Acid	1.2	100 - 101

[0062] The boiling point (°C) of the azeotropic preparation formed from water, dipropyleneglycolmono-n-propylether and the indicated compounds is also given in Table II.

[0063] The invention will be explained by the following examples without however  
5 being limited thereto.

#### Example 1

[0064] The drum of the cleaning device 12 described above was charged with to-be-cleaned material. The material, consisting of textiles, was treated in the first step under liquid cleaning conditions with azeotropic preparations at elevated temperatures. The azeotropic  
10 preparations and the respective treatment temperatures are indicated in Table I above. The material was immersed in the warm azeotropic preparation while being moved. The warm azeotropic preparation was fed in a closed loop from the drum of the cleaning device 12 through a filter device 16 and delivered to the precipitation chamber 4. In the filter device 16, predominantly inorganic fouling (salts) precipitated, which was drawn off. In the precipitation  
15 chamber 14, predominantly fat-containing fouling precipitated, which was likewise drawn off.

[0065] The first treatment step was followed by a second treatment step, which was also carried out under liquid treatment conditions. Fresh azeotropic preparation (see Table I for the composition; in each run, the azeotropic preparation of the second treatment step had the same composition as that of the first step) was supplied to the drum of the cleaning device 12 at an  
20 elevated temperature. The material was supplied in a second closed loop from the drum of the cleaning device 12 to the precipitation chamber 4 via a filter device 16. The separation of inorganic and organic substances took place in the same way as in the first treatment step.

[0066] The second treatment step was followed by a third treatment step, in which the to-be-treated material was treated with the vapor of the respective azeotropic preparation. This had  
25 the composition (see Table I) typical for the respective azeotropic preparation. After passing through the supply pump, the azeotropic preparation was converted into the vapor phase in a distillation device. The vapor was brought into intimate contact with the to-be-treated material in the drum of the cleaning device 12. Part of the vapor was condensed at the time of contact with

the material. The liquid from the cleaning step occurring after the condensation was removed from the drum and, after passing through the filter device 16, was supplied to the precipitation chamber 4 for separation of the organic substances, where organic contaminants were separated. The vapor, which was not already condensed in the drum of the cleaning device 12, was drawn off from the drum, condensed and (after optional filtration) supplied to the reservoir tank 2 for further usage.

[0067] After drawing off the vapor of the azeotropic preparation, the drum was evacuated, for example to  $10^{-2}$  bar, and the remaining vapor was drawn off in the same way as described above. The warm-treated material released the water and the organic components of the azeotropic preparation in the vacuum, so that it was dry after 10 minutes of vacuum treatment.

[0068] The to-be-treated material was in much better condition than such material that has been treated in the conventional way. Both inorganic and organic fouling substances were entirely removed. The material had no unpleasant odor and an excellent appearance. It could be ironed and/or pressed with good results.

[0069] The third step (vapor treatment) is not necessarily required after liquid cleaning; equally good results as those described above were also achieved without the vapor treatment. It is also possible according to the invention to completely or partially replace the steps of treatment of to-be-cleaned material with liquid azeotropic preparation with steps of treatment with azeotropic preparation in vapor form. Equally good cleaning results were achieved with this procedure as well.

## Example 2

[0070] Defectively-printed circuit boards or templates from the SMD-manufacturing were treated with a three-component mixture made of water, dipropyleneglycolmono-n-propylether and/or an amine compound and/or an N-heterocyclic compound and/or organic acids, such as is shown by way of example in Table II. The three-component mixtures, which were used as the active cleaning liquids, were composed of 90 wt% water,  $(10 - y)$  wt% dipropyleneglycolmono-n-propylether and  $y$  wt% of one of the compounds listed in Table II. The cleaning took place in the spray process.

[0071] The circuit boards and templates, respectively, were treated with the liquid azeotropic preparations for removing SMD adhesive at the boiling points indicated in Table II with usage of ultrasound (ultrasound is not, however, necessarily required for achieving good cleaning results). The azeotropic preparations were in the form of a milky emulsion, which  
5 became almost clear during application of ultrasound. A complete removal of the adhesives took place without the need for providing protective devices in the system, such as for protecting against explosions.

[0072] The cleaning results were considerably better than when using conventional solvents such as butyl acetate or isopropanol. In addition, in the case of the latter two, a  
10 protection of the system from explosions must necessarily be provided for reasons of workplace safety.